

# Ab-initio path integral techniques for molecules

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Path integral Monte Carlo with Green's function analysis allows the sampling of quantum mechanical properties of molecules at finite temperature. While a high-precision computation of the energy of the Born-Oppenheimer surface from path integral Monte Carlo is quite costly, we can extract many properties without explicitly calculating the electronic energies. We demonstrate how physically relevant quantities, such as bond-length, vibrational spectra, and polarizabilities of molecules may be sampled directly from the path integral simulation using Matsubara (temperature) Green's functions (imaginary-time correlation functions). These calculations on the hydrogen molecule ( $H_2$ ) are a proof-of-concept, designed to motivate new work on fixed-node path-integral calculations for molecules.

## I. INTRODUCTION

The quantum Monte Carlo (QMC) method has been extensively used as a powerful technique for calculating some physical properties of many-body systems [1], such as molecules [2, 3], solids [4], and nanostructures [5]. For molecules, it has been reported that the diffusion QMC method can achieve near chemical accuracy within the fixed-node approximation [6, 7].

While variational and diffusion QMC algorithms usually sample only electrons at zero temperature, path integral Monte Carlo (PIMC) can sample both the ions and electrons simultaneously at finite temperature. This is a promising approach to calculate thermal effects in the molecular systems. Additionally, PIMC includes the zero-point motion of the ions, yielding the correct quantum statistical treatment of the motion of light ions at all temperatures.

We note that another approach, coupled electron-ionic Monte Carlo (CEIMC) [8, 9], has been demonstrated in which electrons and ions are sampled in two independent but coupled Monte Carlo algorithms. For the molecule we study in this paper, a comparable CEIMC simulation would have a ground-state variational or diffusion QMC simulation of the electrons that determines the Born-Oppenheimer energy surface. These QMC electron energies would then be used in a path integral simulation for the protons. Because the QMC estimates of ground-state electronic energies have statistical error bars, a penalty-method [8] would be used to partially compensate for non-linear biases when these energies are fed into the ionic path integral Monte Carlo. Ultimately, the CEIMC method requires a fairly accurate determination of total energies at many points on the Born-Oppenheimer surface for many different configurations of the ion positions.

In this paper we address the following issue: by treating electrons and ions in the same path integral sim-

ulation (avoiding the explicit calculation of the Born-Oppenheimer energy surface), can we extract properties of a molecule, such as bond-lengths, vibrational frequencies, and polarizability? These properties are often calculated directly from the Born-Oppenheimer surface, i.e. bond-lengths and vibrational frequencies come from local minima and curvature of the energy surface. Here we treat these properties as expectation values of the electron-ion thermal density matrix. That is, we do not make the Born-Oppenheimer approximation, instead, we sample the electron and ion coordinates in a single path integral. The calculations presented here are a proof-of-concept, demonstrating how to extract physical properties from the PIMC simulations. The question of the relative efficiencies of this approach and CEIMC will have to be left to future calculations on larger systems, most likely requiring some kind of a path-integral fixed-node approximation [10].

In PIMC simulations we can collect various correlation function of the system in imaginary time. These functions, known as finite temperature Matsubara Green's functions, can be transformed from the imaginary-time domain into the imaginary-frequencies through the fast Fourier transform (FFT). Since we want to calculate the physical properties of the systems, the correlation function at real frequency need to be obtained from the imaginary-frequency function. It is possible through the analytic continuation techniques to obtain real-time correlation function from imaginary-time correlation function, since a time-ordered correlation function is an analytic function of the time variable in the complex plane [11]. In other words, the time-correlation function calculated along the imaginary axis can be uniquely analytically continued to the real-time axis.

For the case of the simple and closed correlation function, the analytic continuation of imaginary-frequency correlation function is simply the replacement of  $i\omega_n$  with  $\omega + i\eta$ . But for realistic correlation functions in molecules it is hard to find the closed form of imaginary-frequency correlation function. Therefore analytic continuations need to be performed with numerical methods.

However, the analytic continuation of numerically evaluated correlation functions often leads to grossly ampli-

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fied statistical errors in the real time correlation function. Some numerical methods have been proposed for reducing the statistical errors, such as using Padé approximations [12] or least-squares fitting [13], minimizing a suitably defined potential [14], maximum-entropy [15, 16], and singular value decomposition (SVD) methods [17]. It has been reported that the rotational constant of a molecule can be obtained by fitting imaginary-time correlation function from PIMC data to analytic models of correlation function [18].

In this paper we show that some properties of molecules can be sampled directly from path integral simulations using Matsubara Green's functions. For an accurate treatment of the Coulomb interactions between particles we use a new method to tabulate of the Coulomb density matrix that we have developed. Using correlation functions sampled with the accurate Coulomb propagator, we demonstrate PIMC calculations of the bond length, vibrational frequency, and polarizability of a hydrogen molecule. This calculations are important benchmarks for future calculations on more complicated systems. In particular, we have chosen a simple system without a fermion sign-problem so that we can separate the analysis of correlation functions from questions about the fixed-node approximation.

## II. MONTE CARLO SAMPLING OF PATH INTEGRALS

### A. Monte Carlo Sampling

In thermal equilibrium, the average value of any physical quantity can be calculated from the density matrix. In the coordinate representation, the thermal density matrix of  $N$  particles is defined by

$$\rho(\mathbf{R}, \mathbf{R}'; \beta) = \frac{1}{Z} \langle \mathbf{R} | e^{-\beta H} | \mathbf{R}' \rangle, \quad (1)$$

where  $\beta = 1/k_B T$  is the inverse temperature,  $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$  are the particle coordinates,  $\mathbf{r}_i$  is the position of the  $i$ -th particle, and  $Z = \int \rho(\mathbf{R}, \mathbf{R}; \beta) d\mathbf{R}$  is the partition function.

The average value of any physical quantity  $\mathcal{O}$  can be written

$$\langle \mathcal{O} \rangle = \int d\mathbf{R} d\mathbf{R}' \rho(\mathbf{R}, \mathbf{R}'; \beta) \langle \mathbf{R} | \mathcal{O} | \mathbf{R}' \rangle. \quad (2)$$

In the path-integral formula, in  $N$  slices, we expand the density matrix [19],

$$\begin{aligned} \rho(\mathbf{R}_0, \mathbf{R}_N; \beta) &= \int d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_{N-1} \left( \frac{2\pi\hbar^2\Delta\tau}{m} \right)^{-3/2} \\ &\times \exp \left[ - \sum_{n=1}^N \left( \frac{(\mathbf{R}_{n-1} - \mathbf{R}_n)^2}{2\hbar^2\Delta\tau/m} + \Delta\tau V(\mathbf{R}_n) \right) \right], \end{aligned} \quad (3)$$

where  $m$  is the mass of the particle and the time step is  $\Delta\tau = \beta/N$ . In our molecule simulations  $\Delta\tau = 0.01 \text{ Ha}^{-1}$ . We estimate this high dimensional integral with Metropolis Monte Carlo algorithm, with an efficient multilevel sampling method. For a detailed discussion of PIMC methods, see reference [20].

### B. Accurate Coulomb Action

The primitive approximation to the path integral, Eq. (3), is not correct for attractive Coulomb interactions. Instead, we use an improved quantum action  $U(\mathbf{R}, \mathbf{R}')$  in place of the bare Coulomb potential  $V(\mathbf{R})$ . The use of improved actions is discussed in reference [20].

In order to more accurately describe the Coulomb interactions we have developed a new technique for tabulation of imaginary-time Coulomb Green's function [21], from which we extract the Coulomb action. The Green's function,  $G(\mathbf{r}, \mathbf{r}')$  for two particles in  $N$ -dimensional space satisfies the equation,

$$\left[ -\frac{1}{2\mu} \nabla^2 + \frac{z}{r} \right] G^{(N)}(\mathbf{r}, \mathbf{r}'; \tau) = -\frac{d}{d\tau} G^{(N)}(\mathbf{r}, \mathbf{r}'; \tau). \quad (4)$$

The initial condition is  $G^{(N)}(\mathbf{r}, \mathbf{r}'; 0) = \delta^N(\mathbf{r} - \mathbf{r}')$  and  $\mathbf{r}$  and  $\mathbf{r}'$  refer to the relative separation of two particles with reduced mass  $\mu$ , and  $z$  is the product of the charges. There are several ways to numerically evaluate Green's function, see reference [21]. But each methods has its particular limitation and numerical errors are often more than one percent.

Since the Coulomb potential,  $V(\mathbf{r}) \propto \frac{1}{r}$ , has the symmetry properties, without a partial wave expansion we are able to simple, fast, and highly accurate numerical evaluation of  $G(\mathbf{r}, \mathbf{r}'; \tau)$  using one-dimensional FFT's. The technique relies on Hostler's recursion relation [22, 23], which relates the  $N$ -dimensional Green's function to the 1-dimensional function. The use of an accurate Coulomb action is especially important in chemistry. An analogy can be drawn to the use of accurate integration schemes in molecular dynamics. In the current work, we find that quantities, such as the molecular binding energy and electrical polarizability are especially sensitive to the quality of the tabulated Coulomb action.

## III. ESTIMATORS

### A. Energy and the Virial Estimator

There are several estimators to obtain the total thermal energy of a system. The most widely used energy estimator is the thermodynamic energy estimator, which is obtained by differentiating the partition function with respect to  $\beta$ ,

$$E_T = -\frac{1}{Z} \frac{dZ}{d\beta} = \left\langle \frac{dU_i}{d\tau} \right\rangle, \quad (5)$$

where  $Z$  is the partition function and  $U_i$  is the action. In other words, the thermal energy is an average value of the imaginary-time derivative of the action.

For the calculation of molecules we used the virial energy estimator. The virial estimator of the energy is

$$E_V = \left\langle \frac{dU_i}{d\tau} - \frac{1}{2} F_i \Delta_i \right\rangle, \quad (6)$$

where  $\Delta_i$  is the deviation of the  $i$ -th particle from its average position, and  $F_i$  is a generalization of the classical force,

$$F_i = -\frac{1}{\tau} \nabla_i (U_{i+1} + U_i). \quad (7)$$

For more detailed derivation, see references [20] and [24].

## B. Static polarization

The general description of the static polarization of molecules is  $\mathbf{P} = \alpha_{\mu\nu} \mathbf{E}$ , where  $\mathbf{E}$  is the applied electric field,  $\alpha_{\mu\nu}$  is the static polarizability tensor of the molecule, and  $\mu$  and  $\nu$  denote vector directions. For diatomic molecules, symmetry reduces the polarizability tensor to reduced into two components, the parallel ( $\alpha_{\parallel}$ ) and perpendicular ( $\alpha_{\perp}$ ) polarizability.

Using the polarization estimator

$$\alpha_{\mu\nu} = \frac{1}{E_\nu} \sum_i \langle eX_\mu(i) \rangle, \quad (8)$$

we calculate the static polarizability of the molecules given the electric field. Here  $X_\mu(i)$  is the position of the  $i$ -th particle in the direction of  $\mu$ , and  $E_\nu$  is the magnitude of the the electric field in the  $\nu$  direction.

## C. The Matsubara Green's function method

The Matsubara Green's function method is a very useful technique for calculating the physical properties of many-body systems at finite temperature [25]. The general definition of temperature Green's function is

$$G(\tau, \tau') \equiv -\langle T_\tau \mathbf{A}(\tau) \mathbf{B}(\tau') \rangle_\beta, \quad (9)$$

where  $T_\tau$  is the time-ordering operator,  $\tau$  represent the imaginary time, and  $\mathbf{A}$  and  $\mathbf{B}$  are operators. The bracket means the thermal average value at the inverse temperature  $\beta = 1/k_B T$ . If the Hamiltonian of the system is independent of time, Green's function becomes only a function of the time difference  $\tau - \tau'$ , so it also can be written  $G(\tau) = -\langle T_\tau \mathbf{A}(\tau) \mathbf{B}(0) \rangle_\beta$ .

A Fourier transform gives the frequency dependence of Green's function for bosonic quantities, such as molecular vibrations and polarizabilities,

$$G(i\omega_n) = \frac{1}{\beta} \int_0^\beta d\tau e^{i\omega_n \tau} G(\tau), \quad (10)$$

where  $\omega_n = 2n\pi/\beta$  and  $n = 0, \pm 1, \pm 2, \dots$ . In the linear response theory, the linear response of the system to a small perturbation can be written in terms of the Green's function.

As mentioned in the introduction section, through analytical continuation, Matsubara Green's function of complex frequencies,  $i\omega_n$ , can be analytically continued to real, time-ordered correlation functions, which determine physical properties of the dynamic system. However, in numerical analytic continuation even small noise on imaginary-time correlation can make big statistical errors in real time dynamics of the system [17]. Instead of that, we analyze directly the imaginary-time correlation function calculated by path integral Monte Carlo method in order to obtain some properties of molecules. To calculate bond-length and vibrational frequency, we use displacement-displacement imaginary-time correlation functions and their Fourier transforms. For polarizability of molecules we use polarization-polarization correlation function.

### 1. Bond-length and vibrational frequency

For calculating of the bond-length and vibrational frequencies of molecules we use the displacement-displacement correlation function. The displacement correlation function of a harmonic oscillator, with  $V(x) = \frac{1}{2} m \omega_{\text{SHO}}^2 x^2$ , in the imaginary-time domain at the inverse temperature  $\beta$  can be written

$$G(\tau) = -\langle T_\tau x(\tau) x(0) \rangle_\beta, \quad (11)$$

where  $x(\tau)$  refers to the displacement of the oscillator from equilibrium. For  $\tau > 0$ , this correlation function is [26],

$$G(\tau) = -\frac{1}{2m\omega_{\text{SHO}}} \left[ (N+1)e^{-\omega_{\text{SHO}}\tau} + N e^{\omega_{\text{SHO}}\tau} \right], \quad (12)$$

where  $N = 1/(e^{\omega_{\text{SHO}}\beta} - 1)$  is the distribution function at the temperature,  $k_B T = 1/\beta$  and we set  $\hbar = 1$ .

For the hydrogen molecule, the displacement  $x(\tau)$  represents the deviation from the equilibrium separation distance between two protons. The mass,  $m$  is the reduced mass of two protons. At low temperature, we assume that the molecule is in harmonic motion, so we compare our results with the simple harmonic oscillator.

We are able to extract the bond length from imaginary-time displacement-displacement correlation function, Eq. (11). The function  $G(\tau) = -\langle x(\tau)x(0) \rangle$  can measure the fluctuation in the quantity  $x$ . At  $\tau = 0$ , the initial value of  $G(0)$  is the equilibrium average  $-\langle x^2 \rangle$ . As time goes on, the correlation function shows the time decay which measure how  $x(\tau)$  and  $x(0)$  are correlated each other. In the long time limit, the correlation function becomes totally uncorrelated so that the correlation function can be written as,

$$G(\tau \rightarrow \infty) = -\langle x(\tau) \rangle \langle x(0) \rangle \quad (13)$$

At  $\tau = \beta/2$ ,  $G(\beta/2)$  is approximately  $\langle D \rangle^2$ , where  $D$  is the bond length of the molecule at low temperature. Since the bond length can be directly computed as a time-independent average, this limit is an important sanity check on our imaginary-time data.

To obtain the vibrational frequency of molecules we use imaginary-frequency correlation function. Using Eq. (10), we can obtain the correlation function of the simple harmonic oscillator in the imaginary-frequency space,

$$\begin{aligned} G(i\omega_n) &= \frac{1}{\beta} \left[ \frac{1/m}{(i\omega_n)^2 - \omega_{\text{SHO}}^2} \right] \\ &= \frac{1}{\beta} \left[ \frac{-1/m}{(\omega_n)^2 + \omega_{\text{SHO}}^2} \right] \end{aligned} \quad (14)$$

Once we have the correlation function, we can calculate the vibrational frequency  $\omega_{\text{SHO}}$  at  $i\omega_n = 0$ ,

$$\omega_{\text{SHO}}^2 = -\frac{1/(\beta m)}{G(i\omega_n = 0)} \quad (15)$$

at each temperatures  $\beta$ .

Another way to find the frequency is to directly use the correlation function. Since the correlation function  $G(i\omega_n)$  forms a Lorentzian in the imaginary axis of complex Green's function, the full width at half maximum (FWHM) of the correlation function is equal to the frequency of the harmonic oscillator. Therefore we can compare to these frequencies using two methods.

## 2. Polarization

We use the polarization-polarization correlation function to calculate the polarizability of molecules. The imaginary-time correlation function can be written

$$\alpha_{\mu\nu}(\tau) = -\langle T_\tau P_\mu(\tau) P_\nu(0) \rangle, \quad (16)$$

where  $P_\mu(\tau) = ex_\mu(\tau)$ . Once we have obtained the imaginary-time correlation function, by Fourier transform Eq. (10) we can calculate the dynamic polarizability.

Similar to the bond-length calculation, first we calculate the polarizability for a simple harmonic oscillator. (Note that this oscillator is a model for our polarization analysis and is not related to molecular vibrations.) From linear responses theory the static susceptibility  $\alpha$ , due to the small electric field perturbation  $-exE$ , can be written with the first order perturbation theory,

$$\alpha = \frac{2e^2 \langle 0|x^2|0 \rangle}{\omega_{\text{SHO}}} = \frac{e^2}{m\omega_{\text{SHO}}^2} \quad (17)$$

It is clear that the polarizability depends on the confinement potential of the harmonic oscillator,  $\omega_{\text{SHO}}$ .

We can also obtain the polarizability from the imaginary-frequency polarization-polarization correlation function. The correlation function for the simple

harmonic oscillator is

$$\begin{aligned} \alpha(i\omega_n) &= \int_0^\beta d\tau e^{i\omega_n \tau} \langle T_\tau P_\mu(\tau) P_\nu(0) \rangle \\ &= \frac{e^2/m}{(i\omega_n)^2 - \omega_{\text{SHO}}^2}. \end{aligned} \quad (18)$$

Similar to bond length estimator, we assume that the molecules are in the harmonic motion. Once we obtain  $\alpha(i\omega_n)$ , the polarizability  $\alpha(0)$  is the value at  $i\omega_n = 0$ . Note that for molecules the polarizations  $P$  are to be added for all particles in the molecule.

## IV. RESULTS

In this section we report the results of our tests on an  $\text{H}_2$  molecule. Simulations were performed in serial and in parallel jobs with up to eight processors using our open-source `pi` code available online at <http://phy.asu.edu/shumway/codes/pi.html>. We use a time step of  $\Delta\tau = 0.01 \text{ Ha}^{-1}$ , which leads to a discretization of the path integral into 100,000 slices at the lowest temperature (when  $\beta = 10^3 \text{ Ha}^{-1}$  for  $T \approx 300 \text{ K}$ ).

### A. Born-Oppenheimer energy surface

To check the accuracy of our discretized path integral, we calculate the potential energy surface of the ground state  $\text{H}_2$  molecule with the internuclear separation from  $0.5 a_0$  to  $4.5 a_0$ . For this calculation we fixed the proton's position of the  $\text{H}_2$  molecule, then calculate the thermal energy using the virial energy estimator. Figure 1 shows a very good agreement with the accurate potential energy curve (solid line) [27]. Note that we do not use this energy surface for any of the subsequent calculations. We only present the calculation here to verify that we can get the correct detailed energy surface if we so desire. All following results are directly sampled from the electron density matrix.

### B. Vibrational frequency of a $\text{H}_2$ molecule

By sampling the displacement-displacement correlation function in imaginary time, we have calculated the vibration frequencies of a hydrogen molecule ( $\text{H}_2$ ) at three different inverse temperatures,  $\beta = 200, 500$ , and  $1000 \text{ Ha}^{-1}$ , corresponding to  $T \approx 1500\text{K}$ ,  $600\text{K}$ , and  $300\text{K}$ . Figure 2 shows the correlation function in imaginary-frequency domain for a hydrogen molecule. The solid lines are the displacement-displacement correlation functions of imaginary-frequency for the simple harmonic oscillator at each temperatures and the points represent our data points for the Hydrogen molecule. As described in Sec. III C 1, we extract the frequency using two different approaches: (i) a fit to a simple harmonic

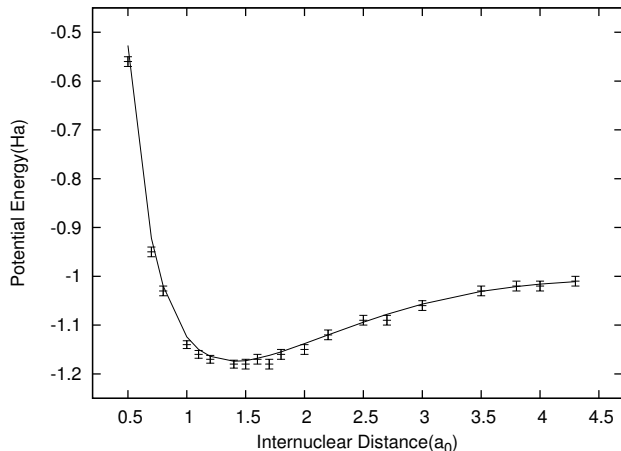


FIG. 1: Born-Oppenheimer surface of  $H_2$  molecule. Solid line is the accurate potential energy curve from the reference [27] and data points are PIMC results using the virial energy estimator.

TABLE I: Vibrational frequencies calculated from PIMC simulations, using a fit to a simple harmonic oscillator (SHO fit) and a measurement of the full-width at half-maximum in the imaginary frequency response.

$\beta(\text{Ha}^{-1})$	T(K)	$\hbar\omega = E_1 - E_0$	
		SHO fit	FWHM
200	1500	0.01866(5)	0.01867
500	600	0.01808(5)	0.01810
1000	300	0.01786((5)	0.01788

oscillator and (ii) the full-width at half-maximum of the frequency response. The results are summarized in Table I.

The exact ground state vibrational frequency of  $H_2$  is 0.02005 in atomic units ( $=4401.21 \text{ cm}^{-1}$ ) [28]. Due to the anharmonic properties of the hydrogen molecule's potential surface, the difference between the ground state and the first excite state level is 0.01895 hartree ( $4161.14 \text{ cm}^{-1}$ ) [29]. The time correlation functions measure this physical energy difference, not the unphysical exact ground state frequency.

It is shown that the frequency is not sensitive to the temperatures. Because the thermal energy is so small, it just affects the rotational levels. Since we doesn't fix the protons in the space, there are rotational effects to the calculation of frequency. The analytical results (solid lines in Fig. 2) are based on the harmonic oscillator without rotational motion.

### C. Bond-length of a $H_2$ molecule

Next, we calculate the bond length of the  $H_2$  molecule from imaginary-time correlation function. Figure 3 shows

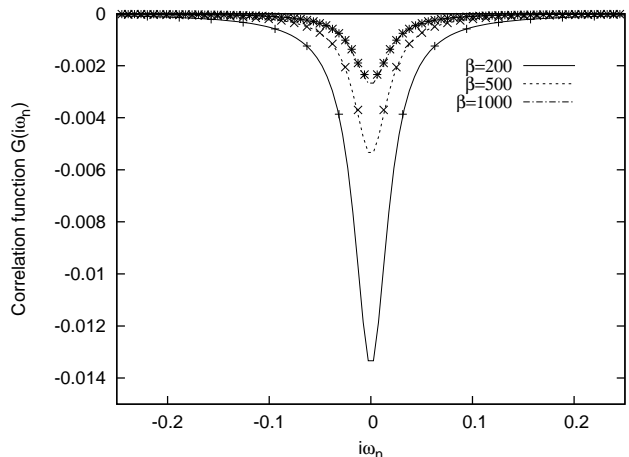


FIG. 2: The displacement-displacement correlation functions of imaginary-frequency for a hydrogen molecule at three different temperatures. The lines are the correlation functions of imaginary-frequency of harmonic oscillator at each temperatures and points represent our results before fitting the vibrational frequency into the correlation function.

the displacement-displacement correlation functions of imaginary time at three temperatures. At room temprature, Fig. 3 (c), we could observe the flat in the middle of the imaginary time, which shows the correlation function is fully uncorrelated.

The exact bond length of a ground state hydrogen molecule is 1.401 in atomic units [28]. With bond-length estimator we directly calculate two average values of the internuclear distance,  $\langle D \rangle$  and  $\langle D^2 \rangle$ . Table II shows the summary of two bond length averages from the estimator and the correlation function of a hydrogen molecule in atomic units. It shows the two different methods agree very well.

The thermal effects on the bond-length of a molecule can be calculated from the Boltzmann factor  $(2J + 1)e^{-\beta E_J}$  with  $2J + 1$ -fold degeneracy due to the rotational motion, where  $J$  is the total angular momentum. The energy is  $E_J = BJ(J + 1)$ , where  $B$  is the rotational constants of a hydrogen molecule,  $B = 60.853 \text{ cm}^{-1}$ . At temperature,  $k_B T = 1/\beta$ , the number of molecules  $N_J$  in the rotational level  $J$  can be calculated by

$$N_J = \frac{(2J + 1)e^{-\beta BJ(J+1)}}{\sum_J (2J + 1)e^{-\beta BJ(J+1)}}. \quad (19)$$

With the number of distribution with respect to the temperature, we can calculate the effective potential due to the rotational motion in explicit method using Morse potential. We observed that the bond-length has changed the factor of  $10^{-2}$ .

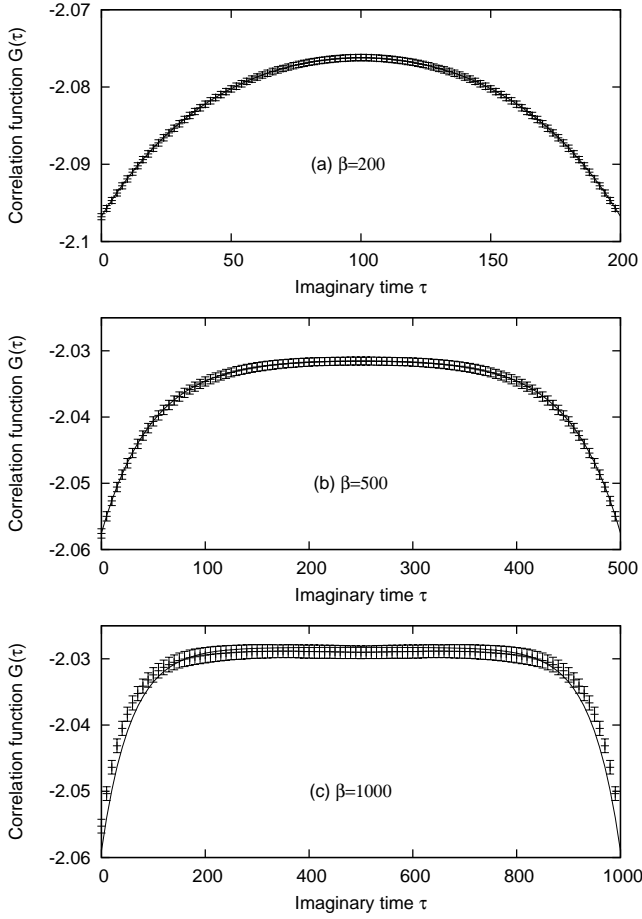


FIG. 3: The displacement-displacement correlation function of imaginary time for a hydrogen molecule at three different temperatures. The solid lines are analytical correlation function of simple harmonic oscillator and the points are PIMC results at each temperatures.

TABLE II: The summary of two bond length averages from the bond-length estimator and the displacement-displacement correlation function of a hydrogen molecule ( $H_2$ ) by path integral simulation (PIMC CF) in atomic units.

$\beta(Ha^{-1})$	T(K)	Bond-length estimator		PIMC CF	
		$\langle D \rangle^2$	$\langle D^2 \rangle$	at $\tau = \beta/2$	at $\tau = 0$
200	1500	2.070(4)	2.101(5)	2.076(1)	2.097(1)
500	600	2.029(4)	2.056(5)	2.031(1)	2.057(1)
1000	300	2.024(4)	2.051(5)	2.029(1)	2.055(1)

#### D. Polarization

Many-body perturbation methods are usually used for calculating the polarizability of molecules. In the case of the hydrogen molecule, the wavefunctions are very well known so that the variational perturbation methods of

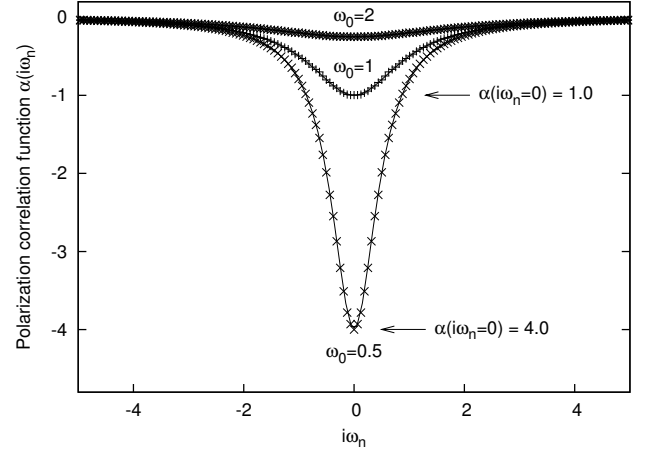


FIG. 4: The polarization-polarization correlation function for simple harmonic oscillators with three different harmonic strength,  $\omega_{SHO} = 0.5, 1, 2$ . At  $i\omega_n = 0$ , the arrows show the polarizability for each oscillators.

the polarizability of the molecule agree very well with the experimental results [30, 31]. With the same method the polarizability have been calculated of the dependence on rotation and vibration states [32] and of the function of internuclear separation [33].

We have calculated the polarizability of a hydrogen molecule in PIMC using two different approaches. The first method is to use the polarization estimator as we explained in the estimator section, see Eq (8). By applying a small electric field through the z-axis to a fixed molecule, we have calculated the polarizability at room temperature, for the parallel direction  $\alpha_{\parallel} = 6.12(50)$ , and for perpendicular  $\alpha_{\perp} = 4.92(26)$  in atomic units. The exact value is  $\alpha_{\parallel} = 6.380$  and  $\alpha_{\perp} = 4.577$  [31].

Another way to calculate the polarizability is to use the polarization correlation function. We calculate the polarizability of the simple harmonic oscillator for three different oscillator strength  $\omega_{SHO} = 0.5, 1, 2$  for the test of the correlation function method. As we mention in the estimator section, the static polarizability can be obtained at  $i\omega_n = 0$  of  $\alpha(i\omega_n)$ . As the harmonic strength increase, the polarizability becomes smaller, see the equation (18). Figure 4 shows that the values of polarizability for the different harmonic strengths exactly follow Eq. (18). The polarizabilities for each oscillators are for  $\omega_{SHO} = 1$ ,  $\alpha = 1$ , for  $\omega_{SHO} = 0.5$ ,  $\alpha = 4$  and for  $\omega_{SHO} = 2$ ,  $\alpha = 0.25$  respectively at  $i\omega_n = 0$ .

We can also estimate the possible dipole transition energy levels ( $\hbar\omega_{SHO}$ ) from the values of the full width at half maximum (FWHM) of correlation function. With the analytic continuation we can obtain retarded Green's function ( $G^R(\omega)$ ) of real frequency ( $\omega$ ) from the imaginary-frequency correlation function ( $G(i\omega_n)$ ). The retarded Green's function is also related the spectral density func-

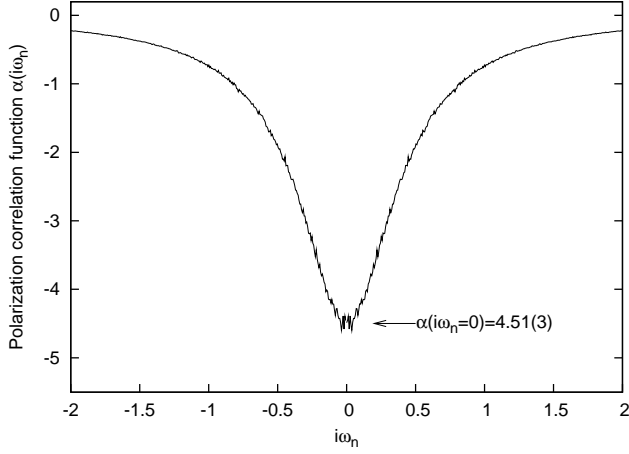


FIG. 5: The polarization-polarization correlation function of a hydrogen atom. At  $i\omega_n = 0$ , the arrow shows the polarizability of a hydrogen atom, 4.51(3). The exact value is 4.5 in atomic units.

tion ( $A(\omega)$ ) for the harmonic oscillator at  $\omega > 0$ ,

$$G^R(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{A(\omega')}{\omega - \omega' - i\eta} \quad (20)$$

$$= \frac{1/m}{(\omega + i\eta)^2 - \omega_{\text{SHO}}^2}.$$

At the poles  $\omega = \omega_{\text{SHO}}$ , the spectral function is a delta function and imaginary-frequency correlation function form a Lorentian with FWHM of  $\omega_{\text{SHO}}$ . Since the harmonic oscillator has one possible transition, the values of FWHM are exactly the same as the harmonic strengths. But for a atom and molecule the FWHM doesn't represent the possible transition levels, because the levels are not equivalent.

Next we test the correlation function method for calculating the polarizability of a hydrogen atom. We found that the polarization-polarization correlation function has the same form whether the proton of the atom is fixed or not. Figure 5 shows the correlation function at  $\beta = 1000 \text{ Ha}^{-1}$ . We have obtained the polarizability is 4.51(3) in atomic units, while the exact value is 4.5.

For the hydrogen molecule, we fixed the positions of two protons at the z-axis, so that the rotation effect doesn't need to be considered for the polarization of the molecule and thus the correlation function is independent of the temperature.

Figure 6 shows the imaginary-frequency correlation function of a hydrogen molecule when the protons are fixed (a) and unfixed (b). For the perpendicular ( $\alpha_{\perp}$ ) and parallel ( $\alpha_{\parallel}$ ) polarizability we need to calculate x,y and z components of the displacement of particles (two electrons and two protons) respectively. We have obtained the perpendicular  $\alpha_{\perp} = 4.56(17)$  and parallel  $\alpha_{\parallel} = 6.40(15)$  polarizability.

The value of FWHM is 0.596 for the perpendicular ( $\alpha_{\perp}$ ) and 0.534 for the parallel ( $\alpha_{\parallel}$ ) of the correlation

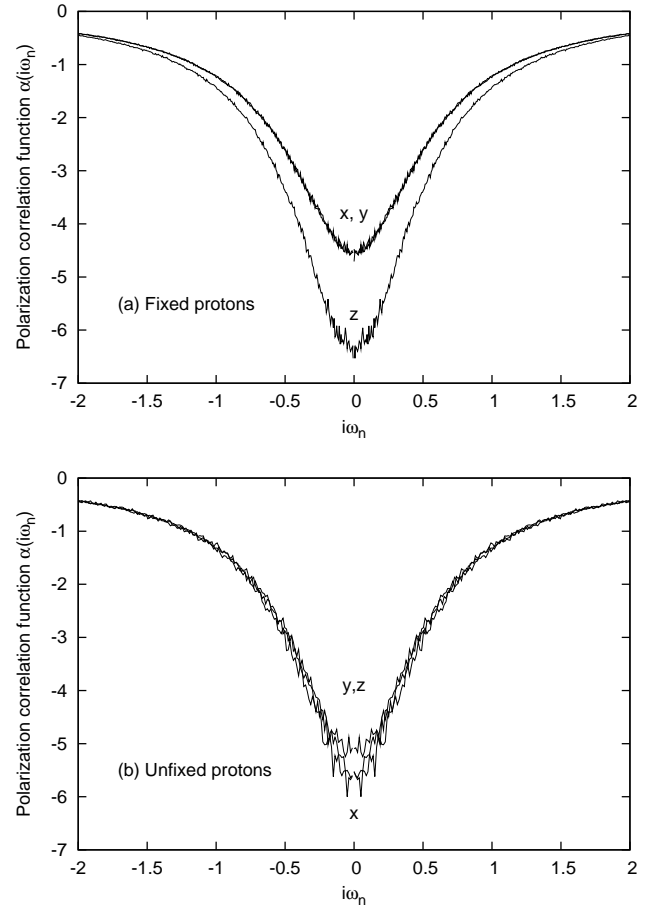


FIG. 6: The polarizability of a hydrogen molecule at  $\beta = 1000$ . The protons are fixed on the z-axis for the upper panel and unfixed at the lower panel. The x, y components and the z component of polarizability represent  $\alpha_{\perp}$  and  $\alpha_{\parallel}$  respectively.

function. The polarizability of a molecule is a physical quantity how the molecule induced by an electric field. For a diatomic molecule possible dipole transition energy levels for ( $\alpha_{\perp}$ ) is bigger than ( $\alpha_{\parallel}$ ) because of the molecule structure.

We also have calculated the correlation function with unfixed protons, allowing rotational and vibrational motion of the molecule. Since the trace of the polarizability tensor is invariant, the average polarizability,  $\alpha = \frac{1}{3}(2\alpha_{\perp} + \alpha_{\parallel})$ , should be identical with different configuration, see Fig. 6 (b). The exact average polarizability is 5.4139 in atomic units [31]. This is the same value of nonfixed protons. Table III shows the summary of the polarizability for the simple harmonic oscillators, the hydrogen atom and the hydrogen molecule.

TABLE III: The summary of the polarizability of simple harmonic oscillators (SHO), a hydrogen atom (H), and a hydrogen molecule ( $H_2$ ) for the fixed and unfixed protons using path integral Monte Carlo method with polarization-polarization correlation function methods (PIMC-CF) in atomic units. The exact data of  $H_2$  are from reference [31].

	$\omega_{SHO}$	PIMC-CF	Exact
SHO	0.5	4.00(6)	4
	1	1.00(6)	1
	2	0.25(6)	0.25
H atom	$\alpha$	4.51(3)	4.5
$H_2$ (fixed)	$\alpha_{\perp}$	4.56(17)	4.577
	$\alpha_{\parallel}$	6.40(15)	6.380
$H_2$ (unfixed)	$\alpha$	5.38(18)	5.413

## V. CONCLUSIONS

We have demonstrated analysis techniques for path integral Monte Carlo simulations of molecules. The aim of these calculations is to show how important physical properties of molecules—energies, bond lengths, vibrational frequencies, and polarizability—can be computed directly from a path integral simulation without an explicit calculation of energies on the Born-Oppenheimer surface. This paper has focused on the analysis of Matsubara Green’s functions for bond length and electrical dipole operators. We have limited this analysis to the  $H_2$  molecule to avoid complications from fixed-node approximations. Future calculations will need to properly treat fermions, most likely with a fixed-node approximation, if these techniques are to have use in practical molecular simulations. The results presented here are benchmarks

that validate continued development of the PIMC technique.

We have two main findings: (1) displacement-displacement Green’s functions can give accurate estimates of the energy splitting  $\hbar\omega$  between the ground and first-excited vibrational states, and (2) dipole-dipole Green’s functions provide accurate estimates of the electrical polarizability of atoms and molecules. Implicit in these results is the demonstration of very high accuracy of the discretized path integral through the use of a carefully tabulated coulomb action.

It is important to the computational strategy we are advocating in these calculations: rather than using costly many-body techniques to calculate individual points on the Born-Oppenheimer surface, we are including the quantum and thermal average of ionic positions in the many-body electronic calculation. This approach may lead to better algorithmic efficiency for systems that have significant thermal or zero-point ionic motion, including systems with strong polaronic effects. The merits of this approach relative to other QMC techniques, such as CEIMC, cannot be measured until we treat larger molecular systems. More complicated molecules will also lead to more complicated Green’s functions that encode information on the normal modes. Nevertheless, the benchmark calculations presented here are a necessary first step towards future calculations on more interesting molecules.

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